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FR 002695540 A JP 020003404 A

(59) Field of Search
UK CL (Edition O) C3P PFE
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(54) Abstract Title
Copolymer for photoresist

(57) A novel copolymer useful for photoresist, which allows a formation of patterns showing a significantly improved resolution in a photolithography using ArF (193 nm) light source, is prepared by copolymerizing at least two cycloaliphatic olefins with an amide or imide (e.g. acrylamide or maleimide derivatives). The cycloaliphatic olefins include norbornene or cyclohexene derivatives.

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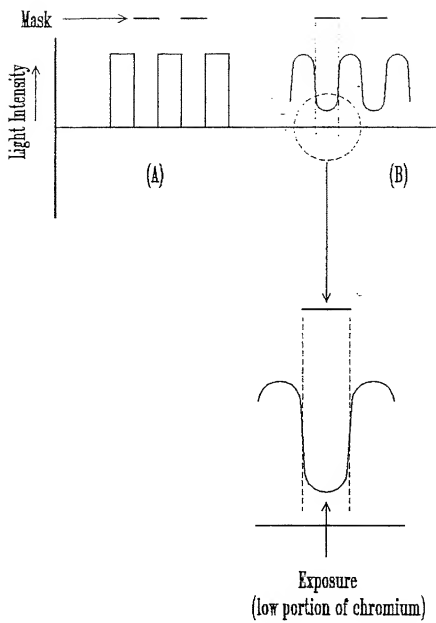


Fig . 1

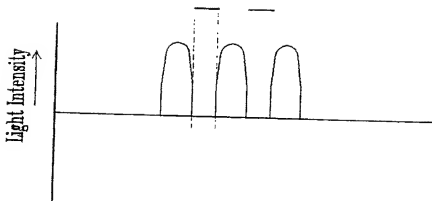


Fig . 2

NOVEL AMIDE- OR IMIDE-INTRODUCED COPOLYMER, PREPARATION THEREOF
AND A PHOTORESIST COMPRISING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a novel amide- or imide-introduced copolymer useful as a photoresist resin in a lithography process using a light source suitable for forming a fine pattern of a highly integrated semiconductor device, a method for preparing the same, and a photoresist comprising the same.

Description of the Prior Art

To achieve high sensitivity in a microlithography for fabricating a semiconductor device, deep ultra violet (DUV) photoresist, a chemical amplification resist, has been the most extensively used recent times. Its composition comprises a photoacid generator and a matrix polymer reacting sensitively to acid.

Ideal photoresist is to satisfy such requirements as transparency to ArF light source, etch resistance, developability in 2.38% tetramethyl ammonium hydroxide (TMAH) and adhesiveness. However, it is very difficult to synthesize a photoresist resin superior in all of the requirements.

For example, a resin having a polyacrylate as a main chain is easy to synthesize but problematic in etch resistance and development. The etch resistance can be increased by introducing aliphatic ring moieties into the main chain.

Although the main chain is of polyacrylate type, with or without on aliphatic ring, problems still remain. The basic principle in the development of the photoresist film used for forming fine patterns of a semiconductor device resides in the

formation of carboxylic acid by the photoacid generator. Because carboxylic acid is better dissolved in 2.38% TMAH than in hydroxy phenol, a solution used for KrF, the thereby produced pattern has a significant problem in that it has a round rather than a rectangular upper portion.

In addition, to overcome the phenomenon that an ArF light source alters the properties of the lens material, a pattern must be formed at a low level of energy because of the high sensitivity to light. To this end, either the amount of the photoacid generator in the photoresist composition or the carboxylic acid content of the photoresist resin must be increased.

Designed as it has been, the prior art solves to both of the above problems because the patterns have a round rather than a rectangular upper portion, making it virtually impossible to obtain a pattern of high resolution.

SUMMARY OF THE INVENTION

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A primary objective of the present invention is to overcome the above problems encountered in prior arts and to provide a novel copolymer useful for photoresist, which allows a formation of patterns having a rectangular rather than a round upper portion, and shows a significantly improved resolution, as well as being superior in etch resistance, thermal resistance and adhesiveness.

An another objective of the present invention is to provide a method for preparing the novel copolymer.

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A further objective of the present invention is to provide a photoresist comprising the novel copolymer.

In accordance with an aspect of the present invention, there is provided a copolymer, prepared by copolymerizing at least two

cycloaliphatic olefins with an amide or imide.

In accordance with another aspect of the present invention, a method for preparing a copolymer for photoresist is provided and comprises copolymerizing at least two cycloaliphatic olefins with an amide or imide at a temperature of about 60-200 °C and at a pressure of about 50-200 atm.

In accordance with a further aspect of the present invention, a photoresist is provided and comprises a copolymer prepared from at least two cycloaliphatic olefins and an amide or imide.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objectives and aspects of the invention will become apparent from the following description of embodiments with reference to the accompanying drawings in which:

Fig. 1 schematically shows an ideal pattern formation and a conventional pattern formation in practice when illuminating light; and

Fig. 2 schematically shows a pattern formation by use of the copolymer according to the present invention.

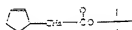
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention contemplates a polymer useful for photoresist, which is a copolymer prepared from at least two cycloaliphatic olefins and an amide or imide.

Preferred examples of the cycloaliphatic olefin moiety include vinylene carbonate, 2-cyclopentene-1-acetic acid, 2-cyclopentene-1-(t-butyl acetate), bicyclo[2,2,2]oct-5-ene-2-t-butyl carboxylate, bicyclo[2,2,2]oct-5-ene-2-carboxylic acid, bicyclo[2,2,2]oct-5-ene-2-(2-hydroxyethyl)carboxylate, 2-(2-hydroxyethyl)carboxylate-5-norbornene, 2-t-butyl carboxylate-5-norbornene, 2-carboxylic acid-

5-norbornene, cyclopentene, cyclohexene, norbornylene, and norbornylene-2-methanol, whose structural formula I are represented as follows:

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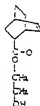
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[vinylene carbonate]

[2-cyclopentene-
1-acetic acid]

[2-cyclopentene-
(t-butyl acetate)]

15



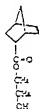
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[bicyclo[2,2,2]
oct-5-ene-2-t-butyl
carboxylate]

[bicyclo[2,2,2]oct-
5-ene-2-carboxylic
acid]

[bicyclo[2,2,2]oct-
5-ene-2-(2-hydroxy
ethyl)carboxylate]

25



[2-(2-hydroxyethyl),
carboxylate-5-
norbornene]

[2-t-butoxy carboxy-
late, 5-norbornene]

[2-carboxylic
acid-5-
norbornene]

30



[cyclopentene]

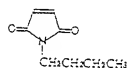
[cyclohexene]

[norbornylene]

[norbornylene-
2-methanol]

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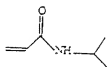
Preferred examples of the amide or imide source for the copolymer of the present invention include N-methylmaleimide, maleimide, N-ethylmaleimide, N-butylmaleimide, N-t-butylmaleimide, N-hydroxymaleimide, acrylamide, N,N-dimethylacrylamide, and N-isopropylacrylamide, whose structural formula II are represented as follows:



[N-methylmaleimide] [maleimide] [N-ethylmaleimide] [N-butylmaleimide]



[N-t-butylmaleimide] [N-hydroxyacrylamide] [acrylamide] [N,N-dimethylacrylamide]



[N-isopropylacrylamide]

The copolymer of the present invention preferably has a molecular weight of 3,000-200,000.

Such two cycloaliphatic olefins and an amide or imide can be
5 polymerized at a high temperature under high pressure in the
presence of a radical initiator. The polymerization can be
achieved through bulk polymerization or solution polymerization.
In this case, a polymerization solvent may be selected from a group
consisting of cyclohexanone, methylethylketone, benzene, toluene,
10 dioxane, dimethylformamide and the mixtures thereof.

For the polymerization, a conventional radical initiator may
be used, which is selected from the group consisting of benzoyl
peroxide, 2,2'-azobisisobutyronitrile (AIBN), acetyl peroxide,
15 lauryl peroxide, t-butylperacetate, t-butyl peroxide, and di-t-
butyl peroxide.

The condition for the polymerization may vary depending on the
properties of the reactant monomers. Preferably, the reaction is
20 carried out at a temperature of 60-200 °C and at a pressure of 50-
200 atm.

A typical manner can be applied for mixing the novel
photoresist copolymer of the present invention with a photoacid
25 generator in an organic solvent to form a photoresist solution
useful for the formation of a positive fine picture image.

Depending on the organic solvent, the photoacid generator, the
lithography condition and the amount of the novel copolymer used
30 may vary. Usually, it is used at an amount of about 10-30 % of the
total weight of the organic solvent.

A detailed description will be given of the formation of
photoresist from the copolymer according to the present invention.

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First, the copolymer of the present invention is dissolved at an amount of 10-30 % of the weight of an organic solvent, e.g. cyclohexanone to which a photoacid generator, e.g. onium salt or organic sulfonium salt, is added at an amount of about 0.1-10 % of the weight of the resist polymer. The resulting solution is filtered through an ultra fine filter, to give a photoresist solution.

Next, the photoresist solution is spin-coated on a silicon wafer and then, soft-baked at a temperature of 80-150 °C for 1-5 min in an oven and heat plate.

Subsequently, using a deep ultra violet stepper or excimer laser stepper, a proper beam is illuminated on the coating which is, then, subjected to post-baking at a temperature of 100-200 °C.

Following this, the exposed wafer is immersed in a 2.38% TMAH aqueous solution for 1.5 min, to obtain an ultra fine positive resist picture image.

Since the novel copolymer for photoresist has a main chain from which the amide or imide moieties dangle directly, they do not move even after the post-baking.

Upon the post-baking, since the amount of the acid is sufficiently more than that of the amide or imide at the photoresist film layer of the quartz part which receives light, the acid diffuses thereat. In contrast, at the photoresist film layer of the chrome part which is insufficiently exposed to the light, the diffusion of the acid is restrained by the amide or imide, giving the same effect as shown in Fig. 2. As a result, the resolution of the pattern is increased considerably.

The amide or imide moieties attached directly to the main chain of the photoresist polymer of the present invention, although

absorbing ArF light, does not have a deleterious influence on the pattern formation because it is used at a smaller amount than the photoacid generator.

5

EXAMPLE

Synthesis of the Copolymer

10 Equi-moles of 2-(2-hydroxyethyl)carboxylate-5-norbornene, 2-t-butoxy carboxylate-5-norbornene and 2-carboxylic acid-5-norbornene and N-methylmaleimide were subjected to a polymerization reaction under a nitrogen atmosphere in a high pressure reactor in the presence of di-t-butylperoxide, an initiator. This polymerization was carried out at various pressures, e.g. 50, 60, 70, 80, 90 and
15 100 atm. A production yield of about 40% was obtained at a pressure of about 80 atm while a yield of about 60% at a pressure of about 100 atm.

20 As described hereinbefore, the novel amide- or imide-introduced copolymer according to the present invention allows the photoresist to be formed into a pattern having rectangular upper parts rather than round ones, upon the development of TMAH, giving rise to an increase in resolution.

25 The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation.

30 Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be practiced in ways other than those specifically described.

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WHAT IS CLAIMED IS:

1. A copolymer for photoresist, prepared from at least two cycloaliphatic olefins and an amide or imide.
- 5 2. A copolymer for photoresist in accordance with claim 1, wherein the copolymer has a molecular weight of 3,000-200,000.
3. A copolymer for photoresist in accordance with claim 1,
10 wherein the cycloaliphatic olefins are selected from a group consisting of vinylene carbonate, 2-cyclopentene-1-acetic acid, 2-cyclopentene-1-(t-butyl acetate), bicyclo[2,2,2]oct-5-ene-2-t-butyl carboxylate, bicyclo[2,2,2]oct-5-ene-2-carboxylic acid, bicyclo[2,2,2]oct-5-ene-2-(2-hydroxyethyl)carboxylate, 2-(2-
15 hydroxyethyl)carboxylate-5-norbornene, 2-t-butyl carboxylate-5-norbornene, 2-carboxylic acid-5-norbornene, cyclopentene, cyclohexene, norbornylene, and norbornylene-2-methanol.
4. A copolymer for photoresist in accordance with claim 3,
20 wherein the copolymer has a molecular weight of 3,000-200,000.
5. A copolymer for photoresist in accordance with claim 1, wherein the amide or imide is selected from a group consisting of N-methylmaleimide, maleimide, N-ethylmaleimide, N-butylmaleimide,
25 N-t-butylmaleimide, N-hydroxymaleimide, acrylamide, N,N-dimethylacrylamide, and N-isopropylacrylamide.
6. A copolymer for photoresist in accordance with claim 5,
30 wherein the copolymer has a molecular weight of 3,000-200,000.
7. A method for preparing a copolymer for photoresist, comprising copolymerization of at least two cycloaliphatic olefins with an amide or imide.
- 35 8. A method in accordance with claim 7, wherein the

copolymerization is carried out at a temperature of about 60-200 °C and at a pressure of 50-200 atm.

9. A photoresist, comprising a copolymer of at least two
5 cycloaliphatic olefins and an amide or imide.



Application No: GB 9711806.1
Claims searched: 1-9

Examiner: Martin Price
Date of search: 29 September 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3P - PFE

Int Cl (Ed.6): C08F 220/52, 220/56, 232/04, 232/08

Other: Online - WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Accession Number 94-227160[28], & FR 2695540 (Elf) - see abstract	1 at least
X	WPI Accession Number 90-049159[07], & JP 02003404 (Mitsubishi) - see abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.